

PATENT SPECIFICATION

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(54) DETERGENT COMPOSITION

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

10 The invention relates to liquid aqueous detergent compositions containing stable, suspended particles which disintegrate when the composition is diluted with water.

15 Liquid or gel detergent compositions containing suspended particles such as globules or capsules containing a beneficial ingredient have been prepared, but difficulty has been experienced in devising a system which is not cloudy or opaque and in which such
 20 particles are completely stable in that they do not dissolve, shrink, disintegrate or lose their contents while retaining the desired property of dissolving or disintegrating, and thereby releasing their contents, when such
 25 compositions are diluted with water under conditions of use.

We have now discovered that by careful selection of ingredients, we can obtain a detergent composition which is clear and which is capable of stably suspending particles that dissolve or disintegrate when the composition is diluted with water.

30 Accordingly, the invention provides an aqueous detergent composition comprising a clear liquid phase having suspending properties, comprising from 1—45% by weight of a detergent active organic material and having dispersed and suspended therein 0.5 to 5 mm sized particles of
 40 hardened carragheenan or hardened high methoxyl pectin that is pectin containing an average of more than 12% methoxyl and a water-dispersible pigment, the particles having the ability to disintegrate
 45 when the composition is diluted with water

thereby to release the water-dispersible pigment.

The clear liquid phase of the composition contains an aqueous organic detergent. Suitable detergent active organic materials 50 are anionic surface active agents, for example ethoxylated lauryl sulphate, ammonium lauryl sulphate and alkanolamine lauryl sulphate such as mono- and triethanolamine lauryl sulphate, nonionic surface active agents, for example nonyl phenol condensed with 12 molecules of ethylene oxide, cationic surface active agents, for example lauryl trimethyl ammonium chloride and amphoteric surface 60 active agents, for example substituted imidazolines, or mixtures thereof. This is not intended to be an exhaustive list and the choice of detergent in the liquid phase is not critical to the invention, provided it does not give rise to loss of optical clarity and that the particles are stable therein. 65

The amount of organic detergent which is present in the liquid phase is at least 1% and is preferably 10—45% by weight. 70

In some circumstances it is desirable also to include the liquid phase an electrolyte: this may function to enhance the suspending properties of the liquid phase or to stabilise the particles against interaction with the detergent active in the liquid phase. The amount of the added electrolyte which can be included in the liquid phase for either of these reasons, is usually at least 0.5% by weight of the composition but will generally not exceed 5%. Suitable electrolytes for this purpose are ones capable of providing a source of sodium, potassium, calcium, ammonium or alkanolamine ions. 85

The composition of the liquid phase should be such that it is capable of suspending the particles in a spatially stable manner for a period of at least 6 months under normal conditions of storage or 90

transport. This can be achieved by intermicellar structuring due to careful selection of the detergent used, or by the addition of organic structuring agents such as Carbopol 941 (water soluble polymer of acrylic acid cross-linked with about 1% of a polyalkyl ether of sucrose and having an average of about 5.8 alkyl groups for each sucrose molecule, the polymer having a molecular weight in excess of 1,000,000) or by employing montmorillonite clays.

According to a preferred embodiment of the invention, the liquid phase is structured by adding to it from 0.5-1.5% by weight of Carbopol 941.

The particles which are suspended and dispersed in the liquid phase are formed from carrageenan or high methoxyl pectin which have been hardened and enclose a water-dispersible pigment. The size of each particle will normally be from 0.5-5 mm.

The particles can be of uniform structure throughout, being composed of either high methoxy pectin uniformly mixed with the hardened carrageenan or the hardened water-dispersible pigment, or they can have an outer wall of carrageenan or high methoxy pectin which encloses a core of liquid or solid ingredients. In this latter case, the water-dispersible pigment can either be present in the wall of the particle, in which case it will be uniformly mixed with other wall materials, or it can be present in the core of the particle.

In order that the particles will resist dissolution or disintegration in the liquid phase of the composition and will enclose the water-dispersible pigment without substantial loss into the liquid phase, the carrageenan or high methoxyl pectin ingredient should be hardened, that is substantially insoluble in the liquid phase, preferably at the time the particles are manufactured, by contacting them with a hardening agent.

The particles are preferably spheroidal in form and will therefore normally have a diameter of from 0.5-5 mm.

Spheroidal particles of the requisite size can be made by any of the known methods, such as are proposed in British patent specification 1 390 503. Whichever method is adopted, the particles when formed are preferably gelled by contacting them with a suitable hardening agent. For example, when carrageenan is used, the hardening agent preferably comprises a solution containing from 1-2.5% by weight of potassium chloride in a 3:1 mixture by weight of ethanol and water. Alternatively, methanol, isopropanol or butanol can be used in place of ethanol. When high methoxyl pectin is used, the hardening agent is preferably an aqueous solution

of ethylene glycol at pH 4, for example 80:20 w/w mixture of ethylene glycol and water.

We have found the water-dispersible pigments can with advantage be enclosed by the particles at a relatively high concentration while retaining the clear character of the liquid phase in which these particles are suspended. This type of composition is accepted as aesthetically more pleasing than a similar composition in which the same amount of pigment is distributed uniformly.

Examples of suitable water-dispersible pigments are Monastral Blue BV, Monastral Green GN V and nacreous pigments such as titanium dioxide-coated mica particles.

The quantity of pigment enclosed within the particles will usually be at least 1%, preferably at least 5% by weight of particles, but the actual amount employed will depend on the desired degree of functionality.

In addition to the ingredients of the liquid phase and the particles herein specified, other ingredients can be included dependent on the intended use of the composition of the invention.

For example, the liquid phase or the particles can additionally comprise perfumes, other pigments, dyes, sequestrants, hydrotropes, oil, bactericides, germicides or pharmaceutical agents.

The compositions of the invention are particularly of value as bath additives which are intended in use to provide a foam and also to colour the bath water.

According to one embodiment of the invention a foam bath additive comprises a clear liquid phase containing a proportion of triethanolamine lauryl sulphate, as the detergent ingredient, structured with Carbopol 941, together with deeply coloured spheroidal particles of hardened carrageenan enclosing a water-dispersible pigment such as Monastral Blue BV. Consumer reaction has indicated that for an aesthetically pleasing appearance, these particles should be uniformly distributed throughout the clear liquid phase and from at least 0.1%, preferably at least 5% by weight of the total composition.

In use, an appropriate portion of the composition is added to bath water to provide the necessary foam and to release the water-dispersible pigment by rupture or dissolution of the particles in the bath water.

The invention is further illustrated by the following Examples.

EXAMPLE 1

Bath additives were prepared as follows:

(i) Liquid Phase

An optionally clear liquid phase was pre-

pared by forming a mixture of the following ingredients:

	% w/w
5 Triethanolamine lauryl sulphate	
(Empicol (TL 40) as 40% solution)	43.0
Industrial methylated spirit	10.0
Carbopol 941	0.9
Triethanolamine	2.3
Water	43.8

10 (ii) *Particles*

Batches of particles in the form of spheroidal capsules containing liquid paraffin of approximately 3—4 mm in diameter, were prepared by the concentric orifice technique using solutions of the following carrageenan as wall materials:

- (a) 2% w/w aqueous solution of Pellugel ID (iota-rich carrageenan) at 20°C.
- 20 (b) 4% w/w aqueous solution of Pellugel ID at 60°C.
- (c) 4% w/w aqueous solution of Auby Gel X52 (iota-rich carrageenan) at 60°C.
- 25 (d) 1% w/w Satiagel GS 350 (Kappa-rich carrageenan) + 2% w/w Auby Gel X52 at 20°C.
- (e) 1% w/w Satiagel GS 350 + 2% Auby Gel X52 + 0.25% locust bean gum formed as a mixture at 60°C.
- 30

Monastral Blue BV, as the water-dispersible pigment was mixed with each of these solutions at a level of 15% by weight and the droplets containing oil were hardened by dropping them into a bath containing 2.5% w/w potassium chloride in a 3:1 mixture by weight of ethanol and water.

Bath additive compositions were then prepared by uniformly distributing the hardened capsules in the liquid phase by gentle stirring.

EXAMPLE 2

45 A bath additive was prepared as follows:

(i) *Liquid Phase*

An optically clear liquid phase was prepared by forming a mixture of the following ingredients:

	% w/w
50 Triethanolamine lauryl sulphate	
(Empicol (TL 40) as 40% solution)	43.0
Industrial methylated spirit	10.0
Carbopol 941	0.9
55 Triethanolamine	2.3
Water	43.8

(ii) *Particles*

60 Batches of particles in the form of spheroidal capsules containing liquid paraffin of approximately 3—4 mm diameter were prepared by the concentric orifice technique from a dispersion of wall material having the following composition:

	% w/w
3% w/w aqueous solution of Satiagel GS 350 (carrageenan)	70
titanium dioxide-coated mica	10
titanium dioxide	2
70 Monastral Blue BV	18
	100

The droplets containing oil were hardened by dropping them into a bath containing 2.5% w/w potassium chloride in a 3:1 mixture by weight of ethanol and water.

A bath additive composition was prepared by uniformly distributing the hardened capsules in the liquid phase by gentle stirring.

EXAMPLE 3

Example 1 was repeated except that the clear liquid phase having suspending properties was prepared by mixing the following ingredients:

	% w/w
Ammonium lauryl sulphate	
(Empicol AL 30)	50.0
90 Hectorite clay	1.5
Sodium chloride	1.5
Water	47.0
	100

EXAMPLE 4

Example 1 was repeated except that the clear liquid phase having suspended properties was prepared by mixing the following ingredients:

	% w/w
Triethanolamine lauryl sulphate	
(Empicol TL 40)	30.0
Carrageenan (Auby Gum X52) as structuring agent	0.75
105 Potassium chloride	0.1
Water	69.15
	100

EXAMPLE 5

A clear liquid phase having suspended properties and based on micellised sodium lauryl ether sulphate was prepared by mixing the following ingredients:

	% w/w
Sodium lauryl ether sulphate	
—26% AD (EMPICOL ESB 3)	48.0
Lauric isopropanolamide	5.0
Lauryl alcohol	5.0
120 Pine oil	10.0
Sodium chloride	2.0
Glycerine	2.5
Industrial methylated spirit	13.0
Water	14.5
	125

Pigment-containing capsules (diameter 4 mm) were prepared from carrageenan as described in Example 1 and suspended in this liquid phase. The proportion of 130

particles present in the composition was about 2.5% w/w.

EMPICOL is a trade mark.

EXAMPLE 6

- 5 Example 1 was repeated except that particle wall material was prepared from a 5% solution of high methoxyl pectin at room temperature; the hardening bath was an aqueous solution of ethylene glycol at pH 4.

A bath additive composition was prepared in a similar manner by mixing hardened high methoxy pectin particles with the same optically clear liquid phase.

15

WHAT WE CLAIM IS:

1. An aqueous detergent composition comprising a clear liquid phase having suspending properties, comprising from 1-45% by weight of a detergent active organic material and having dispersed and suspended therein 0.5-5 mm particles of hardened carrageenan or hardened high methoxyl pectin and a water-dispersible pigment, the particles having the ability to disintegrate when the composition is diluted with water thereby to release the water-dispersible pigment.

2. A composition according to claim 1, in which the detergent active material forms from 10 to 45% by weight of the composition.

3. A composition according to claim 1 or 2, in which the liquid phase additionally comprises an electrolyte.

4. A composition according to claim 3, in which the electrolyte is capable of providing a source of sodium, potassium, calcium, ammonium or alkanolamine ions.

5. A composition according to any preceding claim, in which the liquid phase contains as a suspending agent a water-

soluble polymer of acrylic acid cross-linked with about 1% of a polyallyl ether of sucrose and having an average of about 5.8 allyl groups for each sucrose molecule, the polymer having a molecular weight in excess of 1,000,000.

6. A composition according to any preceding claim, in which the water dispersible pigment comprises at least 1% by weight of the particles.

7. A composition according to claim 6, in which the water-dispersible pigment forms at least 5% by weight of the particles.

8. A composition according to any preceding claim, in which the particles form at least 0.1% by weight of the composition.

9. A composition according to claim 8, in which the particles form at least 5% by weight of the composition.

10. An aqueous detergent composition comprising a clear liquid phase having suspending properties and comprising an aqueous solution a water-soluble polymer of acrylic acid cross-linked with about 1% of a polyallyl ether of sucrose and having an average of about 5.8 allyl groups for each sucrose molecule, the polymer having a molecular weight in excess of 1,000,000, the liquid phase also comprising from 1 to 45% by weight of triethanolamine lauryl sulphate and at least 1% by weight of spheroidal particles of hardened carrageenan enclosing a water-dispersible pigment.

11. A composition according to any preceding claim, which is a foam-bath concentrate.

12. A composition according to any preceding claim, and substantially as described in any one of the Examples.

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